

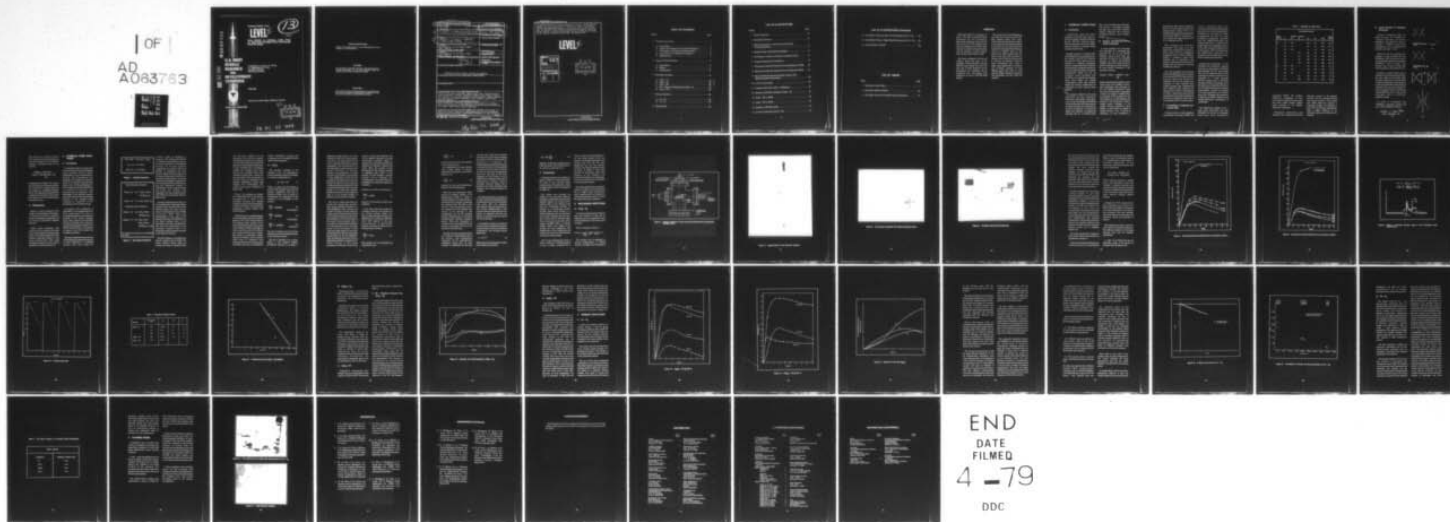
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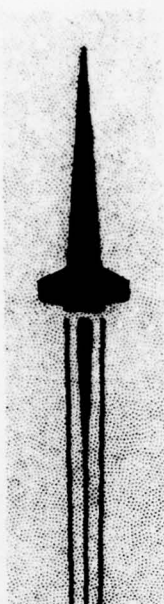
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TECHNICAL REPORT T-78-46

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**FINAL REPORT: (1) CHEMICAL LASER FUELS
(2) REACTIONS BETWEEN ACTIVE CALCIUM AND
SELECTED GASES**

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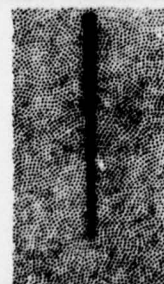
P. Martignoni, O. E. Ayers, J. A. Murfree,
H. A. Nappler and W. M. Chew
Propulsion Directorate
Technology Laboratory



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21. ABSTRACT (Continue on reverse side if necessary and identify by block number) Work on formulation of hydrogen generating solid propellants for chemical lasers and investigation of the reactions of calcium and calcium derivatives with chemical laser effluent gases is described. Formulations of sodium borohydride (NaBH_4) with iron(III) oxide (Fe_2O_3), or ammonium dichromate $[(\text{NH}_4)_2\text{Cr}_2\text{O}_7]$ were prepared and tested as hydrogen gas generating solid propellants. A preliminary examination of amine boranes as hydrogen generators was undertaken. (over)			

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Preliminary studies of the primary reactions of "active" calcium (Ca) with hydrogen (H₂) and nitrogen (N₂) were initiated in support of the Army's chemical pump program for removal of effluent gases from a chemical laser. Also, the secondary chemical pump reactions were investigated. These reactions included: calcium hydride (CaH₂) with N₂; calcium nitride (Ca₃N₂) with H₂, CaH₂ with hydrogen fluoride (HF), and Ca₃N₂ with HF.

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PREFACE

This final report is a summary of work in the area of chemical lasers performed by the Propulsion Directorate during the period of June 1974 to July 1977. The reported work was concentrated in two related areas of study; (a) fuels for chemical lasers, and (b) reactions of active calcium with chemical laser effluent gases.

The Army's emphasis in the area of chemical lasers has been on the hydrogen fluoride/deuterium fluoride (HF/DF) laser system. Therefore, the first area of work reported is on the development of a hydrogen (H_2) or deuterium (D_2) generating solid propellant for use in a HF/DF laser system.

The second area of investigation is the study of the reactions of HF/DF laser effluent gases with active calcium (Ca). The use of active calcium is one method that is being considered by the Army as a way to maintain the required low pressure within the lasing cavity of a HF/DF laser. In this method, the effluent gases from the laser cavity form solid products by reaction with Ca that has been treated to increase its chemical reactivity. Thus, investigation with a time of flight mass spectrometer of primary and secondary reactions of laser effluent gases with active Ca and calcium effluent interaction products was undertaken and the results are reported.

1. CHEMICAL LASER FUELS

A. Introduction

Considerable effort has been expended, in the past three years, to develop hydrogen fluoride/deuterium fluoride (HF/DF) chemical lasers. These lasers depend on the use of high pressure gaseous or cryogenic liquid reactants and diluents.

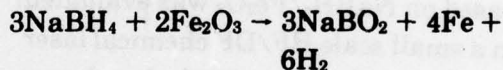
Storable sources of hydrogen (H_2) and deuterium (D_2), in a compact form, are needed for the HF/DF chemical laser system. These sources must be storable in a standby operational mode for long periods of time under the environmental conditions required by the Army. Both storability and safety requirements restrict the use of cryogenic liquid hydrogen and deuterium in an operational chemical laser. Also, safety and weight considerations make high pressure bottled gas sources unattractive for application in Army chemical laser systems.

The primary objective of the work performed by the Propulsion Directorate, Technology Laboratory, was to avoid the storage and handling hazards associated with high pressure or liquid hydrogen by developing an all-solid propellant composition which, upon ignition, can supply the hydrogen gas for a chemical laser.

This solid propellant gas generator will provide a completely storable hydrogen gas source that combines instant readiness with excellent handling behavior and compact storage.

B. Sodium Borohydride/Ferric Oxide Formulation

A solid propellant was developed and evaluated as a hydrogen gas generator for use in the HF/DF chemical laser. [1,2,3] This gas generator is based on the chemical reaction of sodium borohydride ($NaBH_4$) with ferric oxide (Fe_2O_3) to produce hydrogen gas with a purity of 99 mole percent according to the following equation:



Sodium borodeuteride ($NaBD_4$) can be used in place of the $NaBH_4$ to give a solid composition that generates D_2 . For the $NaBH_4$ formulation using Fe_2O_3 , the stoichiometric composition of 26/74 by weight of $NaBH_4/Fe_2O_3$ was selected as the candidate for the development of a solid hydrogen gas generator. This formulation yields 3 weight percent hydrogen or 5.36 weight percent deuterium when $NaBD_4$ is used (28/72 by weight of $NaBD_4/Fe_2O_3$). The volumetric efficiency of this propellant is

equivalent to that of liquid hydrogen since 1 cm³ of the solid propellant will experimentally produce 780 cm³ of hydrogen gas at standard temperature and pressure (STP) as compared to 1 cm³ of liquid hydrogen producing 778 cm³ of hydrogen at STP.

This hydrogen gas generator formulation was found to be very stable with no sensitivity to impact or friction and to have an autoignition temperature above 773°K. In addition, NaBH₄, in contrast to many other hydrides, can be handled in the presence of atmospheric moisture for a limited time and requires no special handling procedures.

The solid hydrogen gas generator based on NaBH₄/Fe₂O₃ was evaluated in a small scale HF/DF chemical laser device as a laser cavity fuel and as a combustor fuel and the results were compared to those obtained from bottled hydrogen gas. Experimental data obtained in this evaluation are summarized in Table 1. Examination of Table 1 clearly shows that the H₂ generated from the solid propellant is equivalent to bottled H₂ when used in an operating HF/DF chemical laser.

C. Formulations Containing Ammonium Salts

A large number of solid propellant formulations containing NaBH₄ and

various ammonium salts were evaluated as potential solid hydrogen gas generators. [4,5] An instrumented combustor was developed for these investigations. [6] The two most promising formulations evaluated were the NaBH₄/(NH₄)₂SO₄ and NaBH₄/(NH₄)₂Cr₂O₇ compositions, [5,6A] These two compositions have a much larger volumetric efficiency and weight percent yield of hydrogen than the NaBH₄/Fe₂O₃ composition and, therefore, are potentially attractive as solid hydrogen gas generators.

Experimental evaluation of the (NH₄)₂SO₄ and (NH₄)₂Cr₂O₇ compositions gave a gas mixture containing approximately 90% H₂, 5% nitrogen (N₂), and 5% ammonia (NH₃) as the combustion products. Tests have been performed on a small screening HF/DF chemical laser to determine the effects of NH₃ in deuterium on the DF laser. It was found that 2% NH₃ in the D₂ will decrease the power output to approximately one-half its original value when compared to pure D₂ as the cavity fuel. Therefore, the production of NH₃ by the NaBH₄/(NH₄)₂SO₄ and NaBH₄/(NH₄)₂Cr₂O₇ formulations is undesirable.

The (NH₄)₂Cr₂O₇ appears to be a much better ammonium salt than (NH₄)₂SO₄ for the use in hydrogen generating solid propellants

Table 1. Summary of Laser Runs

Flow Rates (cm ³ /sec)							
Laser Species	F ₂	Cylinder H ₂	Generator H ₂	D ₂	He	Total	Power (Watts)
DF	379	202	—	566	745	1892	50.9
	380	202	—	571	734	1887	43.5
	380	202	—	571	734	1887	45.9
	379	—	190	566	739	1874	46.4
	380	—	202	566	739	1887	45.9
	380	—	202	566	739	1887	46.6
	380	—	202	566	734	1882	45.9
HF	380	594	—	196	728	1898	6.0
	381	594	—	196	756	1927	5.0
	381	594	—	196	756	1927	5.9
	381	—	661	196	750	1988	5.5
	381	—	683	196	750	2010	6.0

containing NaBH₄. The NaBH₄/(NH₄)₂Cr₂O₇ composition is more easily ignited, produces less ammonia and gives a better "clinker" residue when compared to the NaBH₄/(NH₄)₂SO₄ composition.

Preliminary experiments were carried out in an attempt to reduce the

ammonia content in the gaseous products. The hot combustion gases were passed through a tube packed with either Shell 405 catalyst or aluminum chloride to decompose or react with the NH₃ gas respectively. Only a slight reduction in the ammonia content of the effluent was observed.

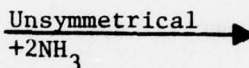
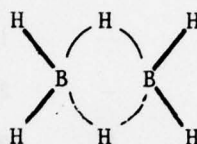
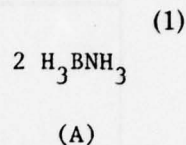
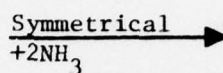
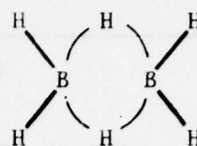
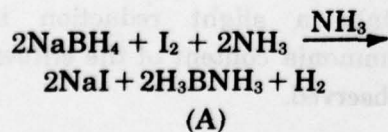
D. Amine Boranes as Hydrogen Generators

A class of compounds called the amine boranes was identified as possible hydrogen generator candidates. [7] Ammonia causes a cleavage of diborane giving both symmetrical and unsymmetrical products, equations 1 and 2.

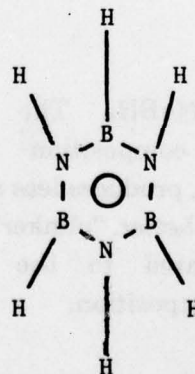
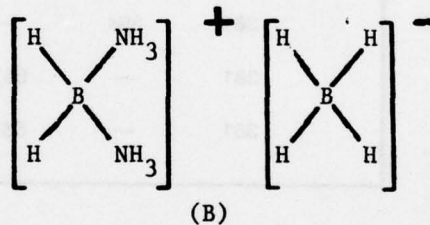
Product B can also undergo substitution to form products such as $\text{H}_2\text{B}(\text{NH}_3)_2\text{F}$. Both A and B are known to lose hydrogen and form the polymer $(\text{H}_2\text{BNH}_2)_n$, upon heating. This polymer upon further heating also loses hydrogen to form borazole, (C).

Borazole is a stable liquid. Loss of hydrogen from borazole should leave the very stable boron nitride (BN). Therefore, either A or B, if formulated correctly could produce three moles of H_2 per mole of BN. Since the hydrogens attached to the boron are hydridic, H^- , these compounds could conceivably be monopropellants, that is, they would decompose with no additional additives needed.

In order to investigate this possibility, a standard reaction was run to form H_3BNH_3 as follows:

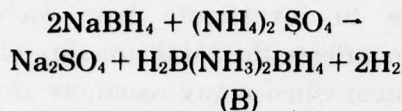


(2)



(C)

This material, A, is soluble in diethyl ether. In order to avoid using diborane to produce product B, it was decided to attempt a synthesis based on the reaction:



Tetrahydrofuran (THF) was used as the reaction solvent. The major product was not soluble in diethyl ether but was soluble in 1,2-dimethoxyethane (GLY). The isolated products from the syntheses were found to burn with a green flame in air when ignited with a hot nichrome wire.

E. Miscellaneous

Based on work conducted on the catalytic decomposition of hydrazine, a concept was conceived to produce a mixture of hydrogen and nitrogen for use as fuel in the HF/DF chemical laser. [8]

NASA Lewis calculations were carried out on the reaction of several cyano compounds such as dicyanoacetylene and tetracyanoethylene with fluorine containing oxidizers. It was found theoretically that large quantities of fluorine atoms could be generated by these reactions. [9]

2. CHEMICAL PUMP REACTIONS

A. Introduction

Considerable effort and money has been spent by the Army High Energy Laser Systems Project Office (AHELSPPO) in a concentrated effort to develop and demonstrate the feasibility of a calcium (Ca) chemical pump in an HF/DF chemical laser system. [10, 11] The development of such a system required the acquisition of necessary scientific and engineering information. The knowledge of the chemical reaction rates and of the reaction mechanisms involved in the chemical pump reactions is essential in the development of the chemical pump.

A proposal was submitted to AHELSPPO in 1975 suggesting that a mass spectrometer be used to investigate the primary and secondary reactions of the calcium chemical pump. These primary and secondary reactions, occurring when calcium is reacted with the gaseous effluent of an HF/DF chemical laser, are presented in Figures 1 and 2. The proposal was accepted and funded.

The time of flight mass spectrometer (TOF) with its four channel analyzer is an ideal instrument to investigate reaction rates when gases are

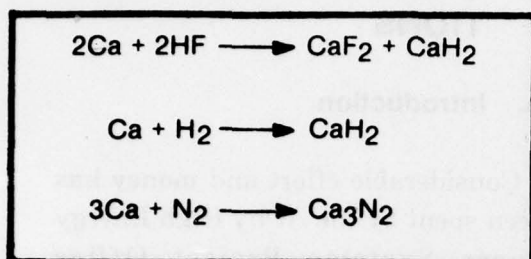


Figure 1. Primary Reactions

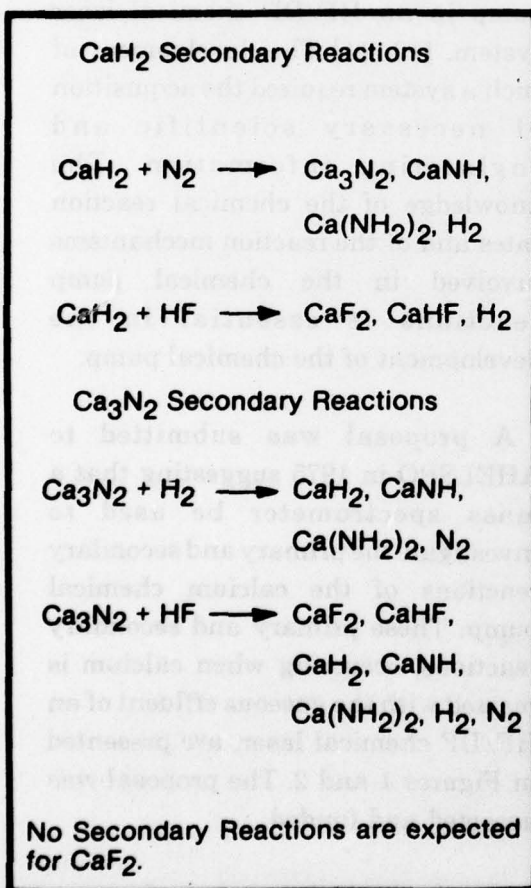


Figure 2. Secondary Reactions.

involved, either as reactants or products, in the reaction. The TOF is an extremely rapid analyzer and can be used to monitor the concentration changes of various gaseous components of the reaction. Thus, it is possible to investigate how each reaction affects the total pressure of the system when many reactions are occurring simultaneously. A reaction chamber was designed in October 1975 for incorporation into the TOF system, and the components ordered. A modification of the original design was made, the chamber was assembled, and the complete system with TOF was successfully tested in March 1976.

It was the original intent to carry out our investigations on the same calcium material used in the fabrication of the chemical pump. The active calcium was to be furnished by the principal contractor, TRW. Thus, the determination of the rates of the primary reactions was scheduled to be the initial starting point of the experimental kinetics investigations. The rates and mechanisms of the secondary reactions were to be determined using the products formed in the primary reactions.

The first attempt to investigate the primary reactions was a failure. The active calcium burned while an attempt was made to transfer it from

the container supplied by the contractor to the reaction chamber. The transfer took place in an ordinary dry box which had been flushed with argon for a considerable period of time. It was concluded that no equipment suitable for handling the active calcium was available. Funds were requested, received and a vacuum dry box was ordered. The vacuum box, as received, was not operational and required modifications which were designed and accomplished. The vacuum box became operational in March 1977.

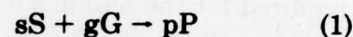
Thus, it was necessary to reorient the original approach to the kinetics investigations. A study of the secondary reactions was initiated using the less active and commercially available secondary reaction starting compounds, calcium hydride and calcium nitride.

Unfortunately, any results obtained from these studies could not be directly applied to the active calcium used in the chemical pump because of the drastically different surface area of the commercially available materials and those materials produced by effluent gas reactions with the active calcium. The method of preparation, surface effects and diffusion rate are factors which must be considered when studying reaction rates between gases and solids. However, it was desired to

obtain preliminary results and conclusions and to completely test the experimental equipment.

B. Theory

The reactions occurring in the chemical pump are heterogenous reactions between a solid, S, and a gas, G, to form a solid product, P:



where s, g, and p are the number of moles of solid reactant, gas and solid product, respectively. The rate of chemical reaction can be found by determining the consumption of the reactants or the formation of the product:

$$\frac{d[G]}{dt} = -k[G]^n[S]^m \quad (2)$$

Consumption

$$\frac{d[S]}{dt} = -k[G]^n[S]^m \quad (3)$$

Consumption

$$\frac{d[P]}{dt} = +k[G]^n[S]^m \quad (4)$$

Production

The use of equation (2) is the most sensitive and accurate method because of the following reasons:

The use of equation 3 or 4 would require a very sensitive thermogravimetric balance to measure a

significant weight change. It is also necessary to use a very small amount of S and a very large amount of G in order to keep the experimental system manageable. The concentration of G will essentially remain constant if the stated conditions are obeyed. However, the introduction of a large quantity of gas will set up currents and a long stabilization period will be required for the balance to settle. The system will also have to be insensitive to high temperatures. Equations 3 and 4 cannot be used if more than one solid product or if a solid and a gaseous product are formed, if a gas mixture is used, or if the reaction product or products are not known accurately.

The use of a mass spectrometer to monitor the reactant gas concentrations during chemical reactions is a well established, rapid, accurate and sensitive technique. In this technique a large amount of solid reactant is used with a minimal quantity of gas so that the contribution of the solid reactant to the reaction rate is constant. Also, if more than one solid product is formed or if the products are not accurately known, the use of equation 2 is still valid since these factors do not enter into the equation. The use of the mass spectrometer can also be extended to study multiple gas reactants with the appropriate changes to equation 2. An added feature of the mass spectrometry technique is that if any

gaseous products are produced, they can be detected. Therefore, the mass spectrometer technique based on equation 2 is the preferred method for studying the reactions of gases with solids. When the amount of gas introduced into the reaction chamber is negligible with respect to the quantity of solid present, a pseudo reaction rate is obtained. The concentration of the solid reactant is considered to be constant during such a reaction.

Equation 2 can then be rewritten as:

$$\frac{d[G]}{dt} = -k^*[G]^* \quad (5)$$

where k^* is the pseudo reaction rate coefficient.

It has been found that under the conditions observed, the reactions of Ca, calcium hydride (CaH_2), and calcium nitride (Ca_3N_2) with the laser effluents H_2 , N_2 , and HF are of the first order with respect to the gas concentrations. A generalized equation may then be written for the chemical pump reactions:

$$\frac{d[G]}{dt} = -k^*[G] \quad (6)$$

this equation can be rearranged and integrated to give:

$$\ln \frac{[G]}{[G_0]} = -k^*t \quad (7)$$

where $[G_0]$ is the initial concentration of the reacting gas, G.

By designating the mass spectrometer output which is directly proportional to $[G]$ as N , we can rewrite equation 7 as:

$$\ln \frac{N}{N_0} = -kt \quad (8)$$

where N , N_0 , and k are substituted for $[G]$, $[G_0]$, and K^* respectively.

There are two phenomena which govern the reaction kinetics of an experimental system in which a specific quantity of a reactant gas is introduced into a chamber containing the reactant solid. The first is the increase of gas concentration due to the expansion into the chamber. The second is the decrease of gas concentration due to the chemical reaction. Initially, both are occurring simultaneously, causing a transient period. After the expansion is complete, only the decrease due to the reaction is occurring. There are two methods to treat the data.

The first and most accurate method is to obtain an experimental trace of the reaction, and subsequently reproduce all the experimental conditions except that an inert material is substituted for the solid

reactant and obtain the expansion trace. Since $[G_0]$ is not really a constant but rather a function of time until the expansion is complete, the experimentally determined expansion trace becomes $N_0(t)$. It is then possible to obtain $\ln N/N_0$ for each t from the reaction trace $N(t)$ and the expansion trace $N_0(t)$. The slope of the linear regression $\ln N/N_0$ versus t is $-k$, the reaction rate coefficient. This type of experimental analysis requires extremely accurate timing and is practical only when automated data collection and analysis systems are available.

The alternate method to determine k is to start the data processing after the transient period is over and to consider some point after the maximum concentration has been reached as N_0 . The obvious disadvantage of this method is that the initial period of the reaction is neglected and that any process occurring during this period will not be detected.

It is possible to obtain the energy of activation from a determination of the reaction rates of a reaction at different temperatures. The Arrhenius theory shows that:

$$k = Ae^{-E_a/RT} \quad (9)$$

Taking the natural logarithm of both sides, yields the following:

$$\ln k = \ln A - \frac{E_a}{RT} \quad (10)$$

Therefore, if the $\ln k$ is plotted against $1/RT$, the slope of the straight line is $-E_a$ and the y intercept is $\ln A$.

C. Experimental

A drawing of the reaction chamber is shown in Figure 3. It was designed for the study of the chemical pump reaction rates and mechanisms using a calcium wafer or pellet to be supplied by TRW, Inc.

The change from studying the primary to the secondary reactions required a modification of the reaction chamber. Figure 4 is a picture of the sample holder of the chamber used with the commercial powders. It consists of a machinable ceramic crucible, either boron nitride or a silicate material (Lava), around which was wound a heating wire. The wire was covered with an alumina paste. Five to seven grams of powder, either calcium hydride, CaH_2 , or calcium nitride, Ca_3N_2 , were added to the crucible for each experiment. The temperatures of the crucible and the powder were monitored with chromel-constantan thermocouples.

Part of the experimental set-up is shown in Figure 5. A definite amount of gas or gases, monitored by a

baratron gauge was introduced into a one liter metal cylinder which was heated to the desired temperature with heating tape. The gas was then introduced into the hot reaction chamber. The hand controlled valves, as shown in Figure 5, were later replaced by pneumatic valves. The pressure in the chamber was monitored by either a 5 or 1 psia gauge. A tube connected the reaction chamber to the mass spectrometer.

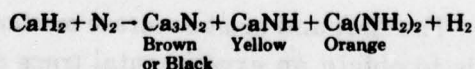
The entire experimental equipment, is shown in Figure 6 and includes the time of flight mass spectrometer, power supplies used for heating and recording equipment used to monitor the temperatures and pressures.

3. SECONDARY REACTIONS

A. $\text{CaH}_2 + \text{N}_2$

A variety of products may be formed from the reaction of CaH_2 and N_2 depending upon the temperature used in the experiment and the extent of the reactions.

Thus, according to Figure 2:



The reaction was investigated at various temperatures. A definite amount of nitrogen was introduced to

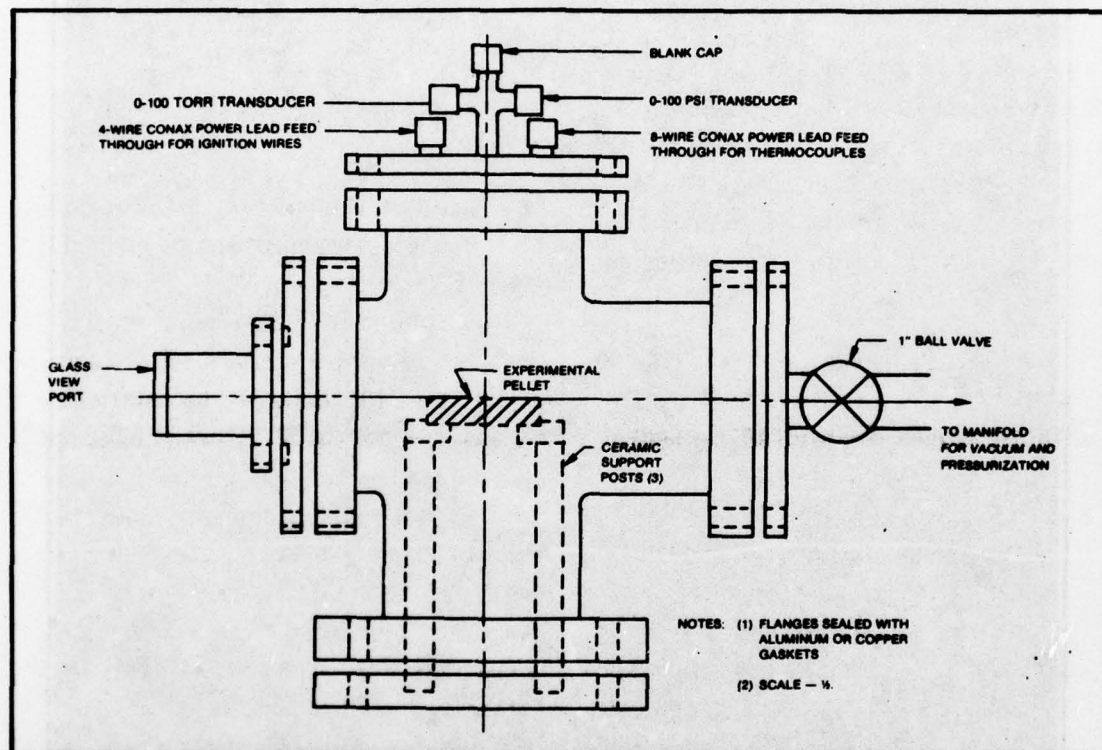


Figure 3. Reaction chamber for laser fuel and chemical pump experiments (October 1975).

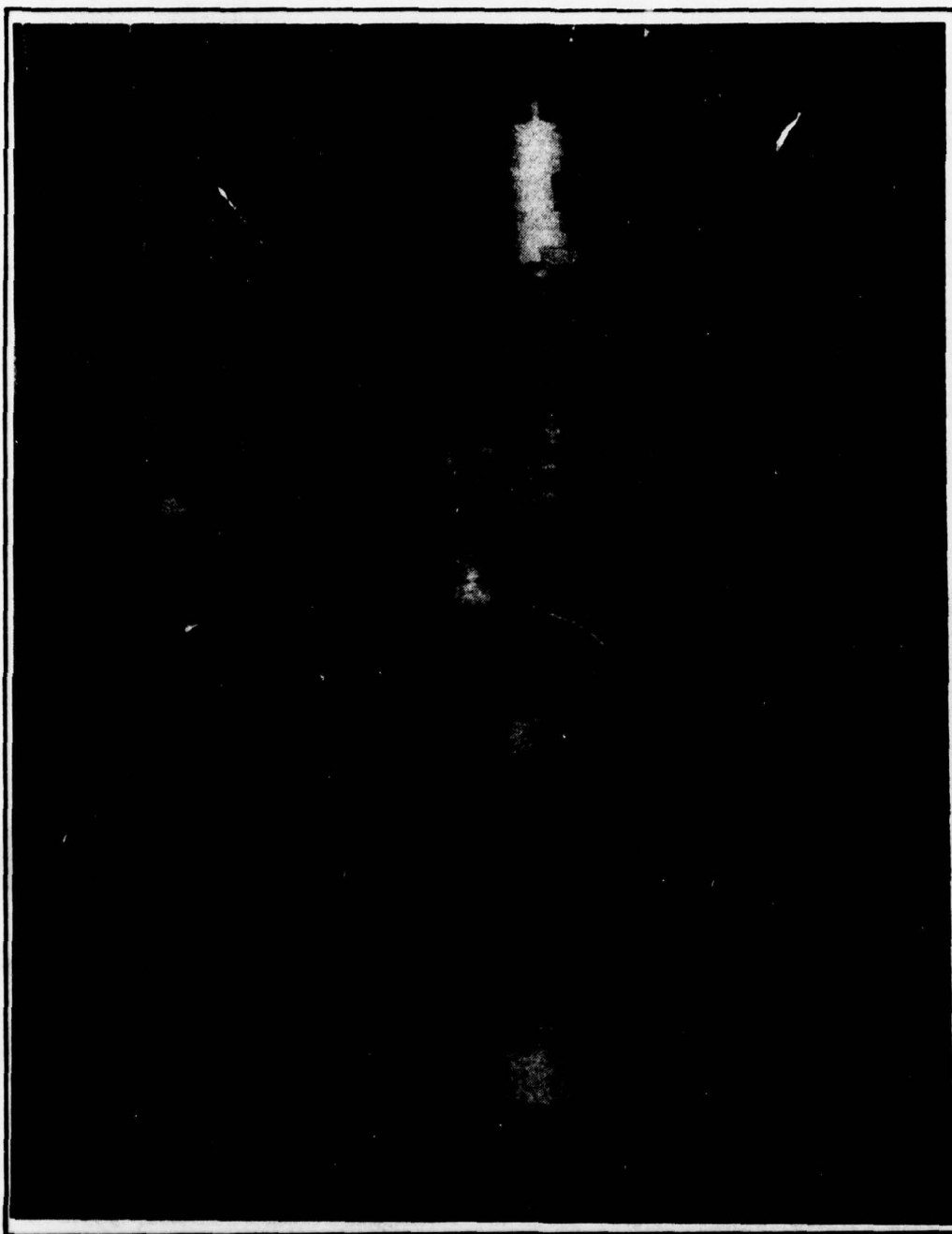


Figure 4. Sample Holder of the Reaction Chamber

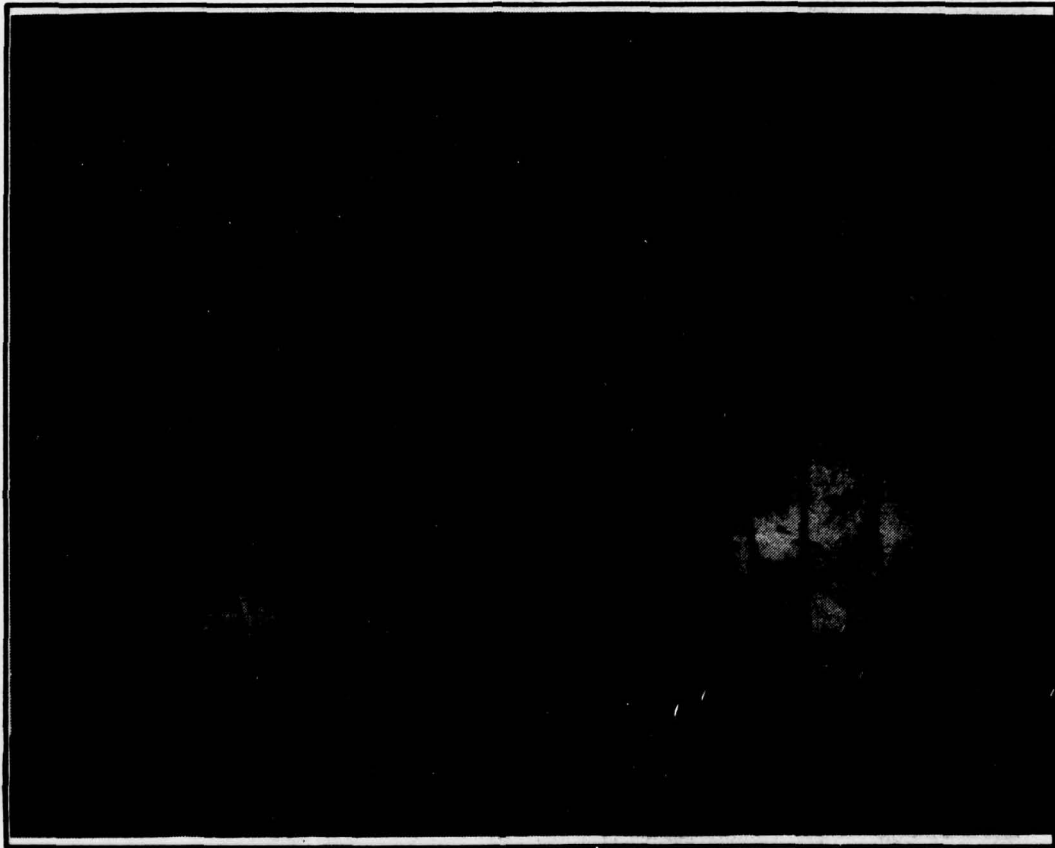


Figure 5. Hot Reaction Chamber With Hand Controlled Valves

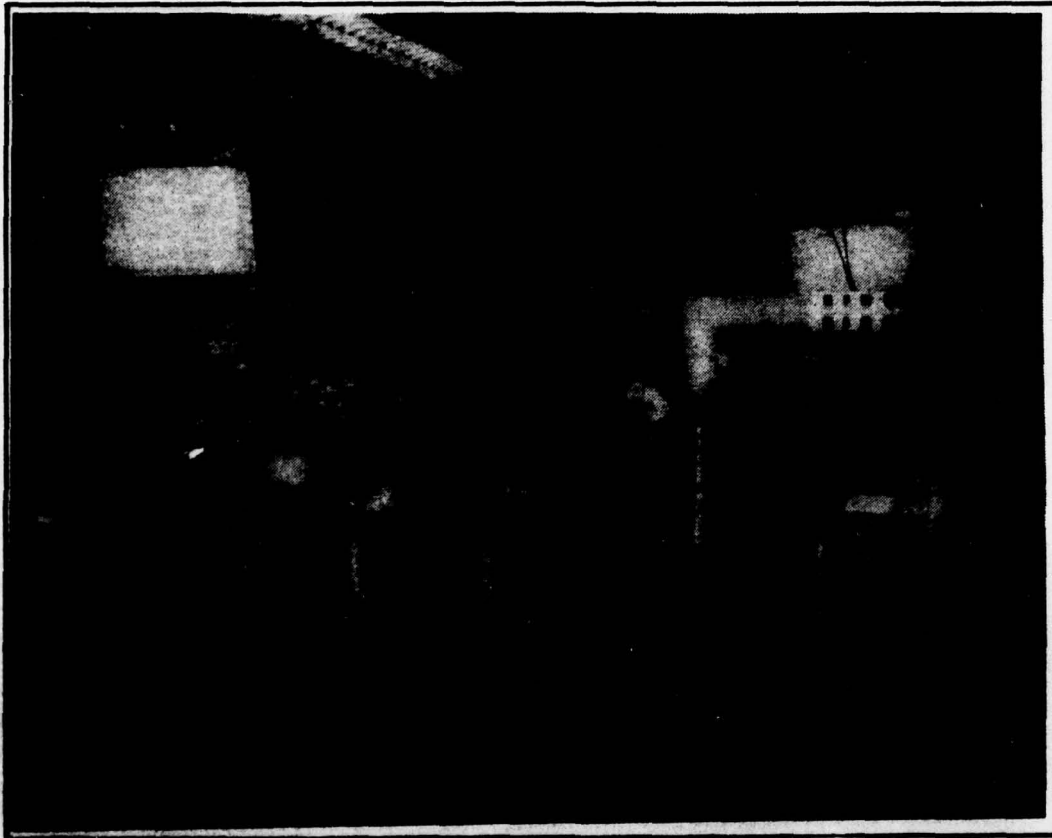


Figure 6. Complete Experimental Equipment

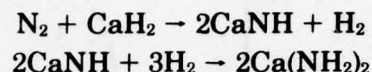
the one liter bulb. The pressure of the gas was maintained between 667 and 933 Pascals (5 and 7 torr) in order that each pulse of gas would react with about one percent or less of the calcium hydride. The valve between the reaction chamber and the metal cylinder was opened and the gas allowed to react with the powder. The hydrogen, H_2 , nitrogen, N_2 , and ammonia, NH_3 , peaks were monitored with the mass spectrometer and the temperature and pressures monitored with appropriate instrumentation.

The first indication of any reaction occurring between N_2 and CaH_2 occurred at 643°K. A set of at least four duplicate runs were carried out at each temperature. Figures 7 and 8 are experimental results obtained from the reaction at 753°K and at 803°K. It is interesting to note that the concentration of the first run reached a peak faster and also dropped faster than subsequent runs. This occurred at both temperatures. The probable explanation for this finding is the fact that as more surface material of the hydride is reacted, the rate of reaction becomes slower due to diffusion effects. [12]

The mass spectrometer outputs of both the H_2 and N_2 concentrations is represented in Figure 9.

There is an almost simultaneous rise in both the H_2 and N_2 concentrations

when N_2 is allowed into the chamber. There is also a simultaneous drop in the concentrations of both gases. A plausible explanation of this observation is that two reactions occur as N_2 is introduced:



These reactions occurred so rapidly that it was impossible to make any attempts to measure reaction rates with the available equipment. Figure 9 definitely establishes the usefulness of a fast monitoring mass spectrometer when studying solid-gas reaction kinetics.

A graph of $\ln N/N_0$ versus time for four consecutive runs carried out at 860°K is shown in Figure 10. The graph was used to determine k , the reaction rate coefficient. The data indicates that the results were reproducible. The numerical values are presented in Table 2.

The Arrhenius plot of the reaction of CaH_2 with N_2 is presented in Figure 11. The different symbols on the graph represent data from two separate experiments.

A value of 19 Kcal/mole for the activation energy of the reaction is obtained from the graph. [13]

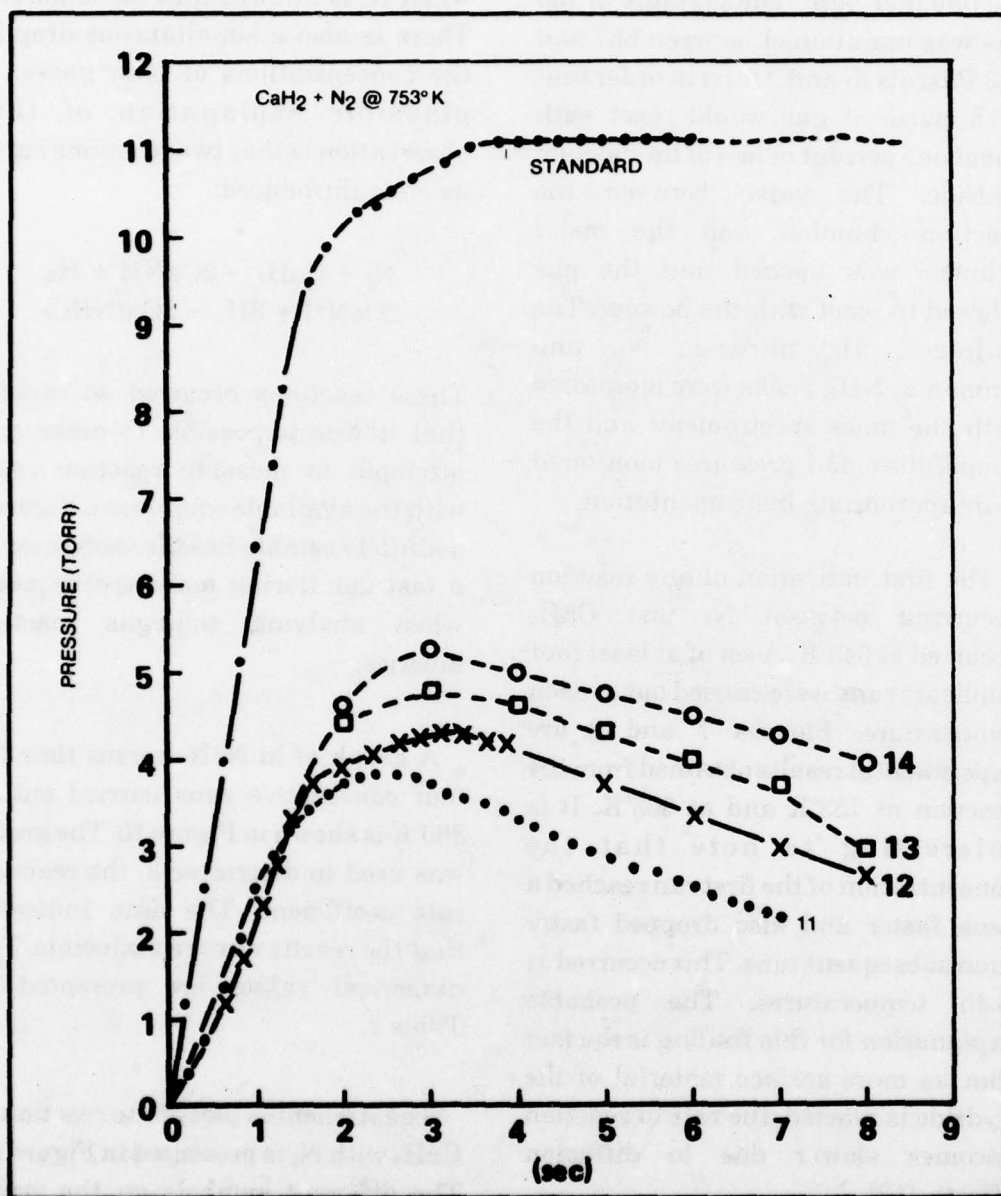


Figure 7. Experimental results obtained from the reaction at 753°K.

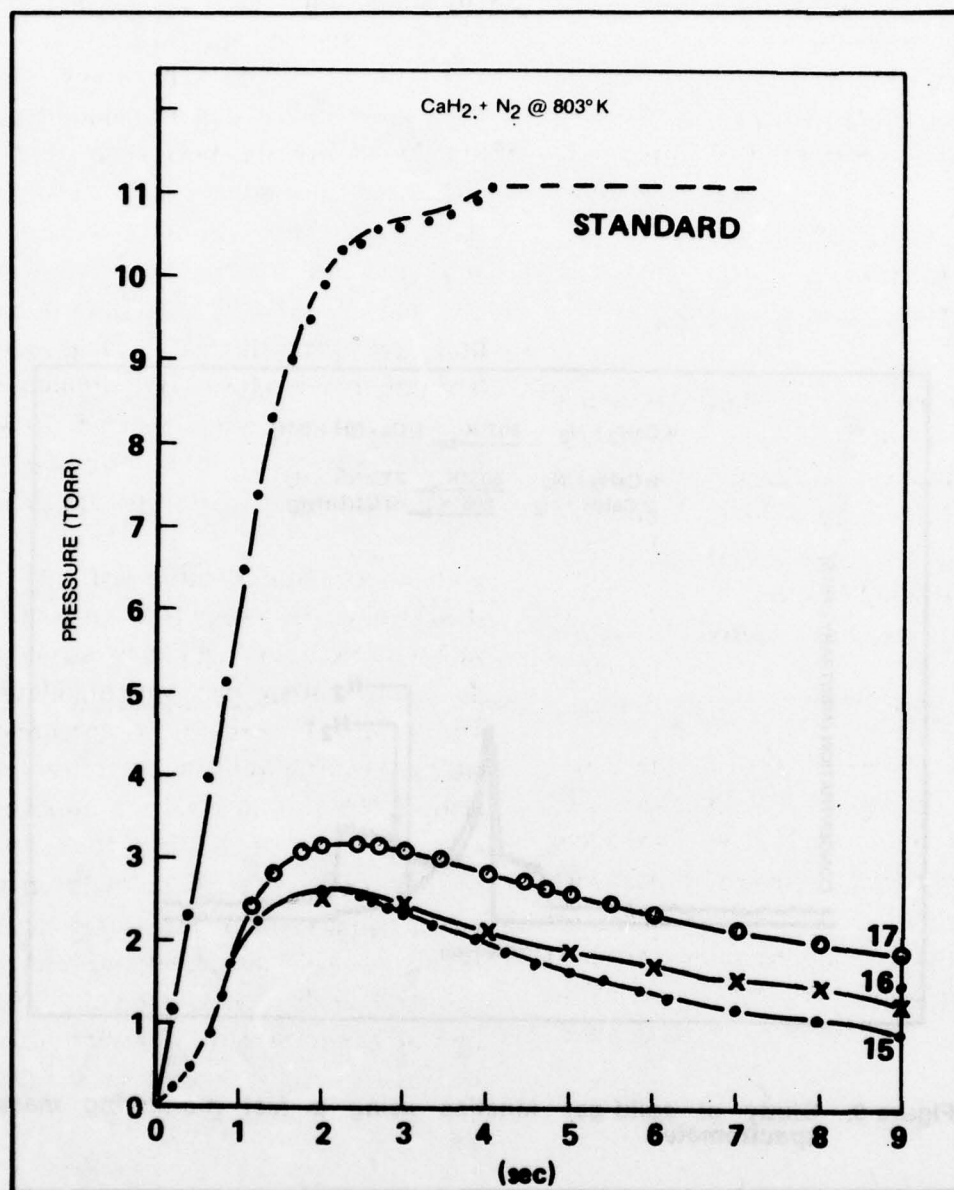


Figure 8. Experimental results obtained from the reaction at 803°K .

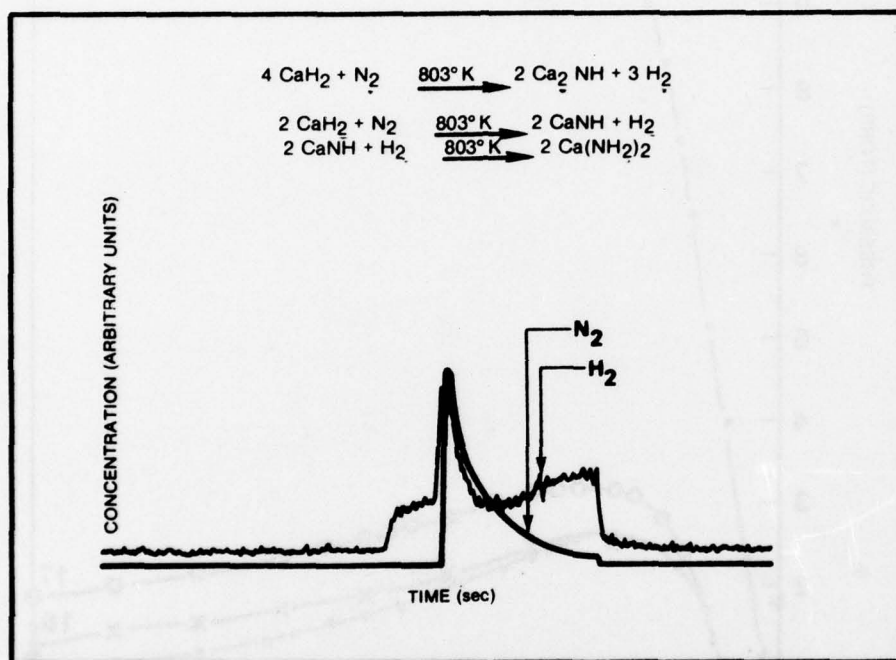


Figure 9. Study of solid-gas kinetics using a fast monitoring mass spectrometer.

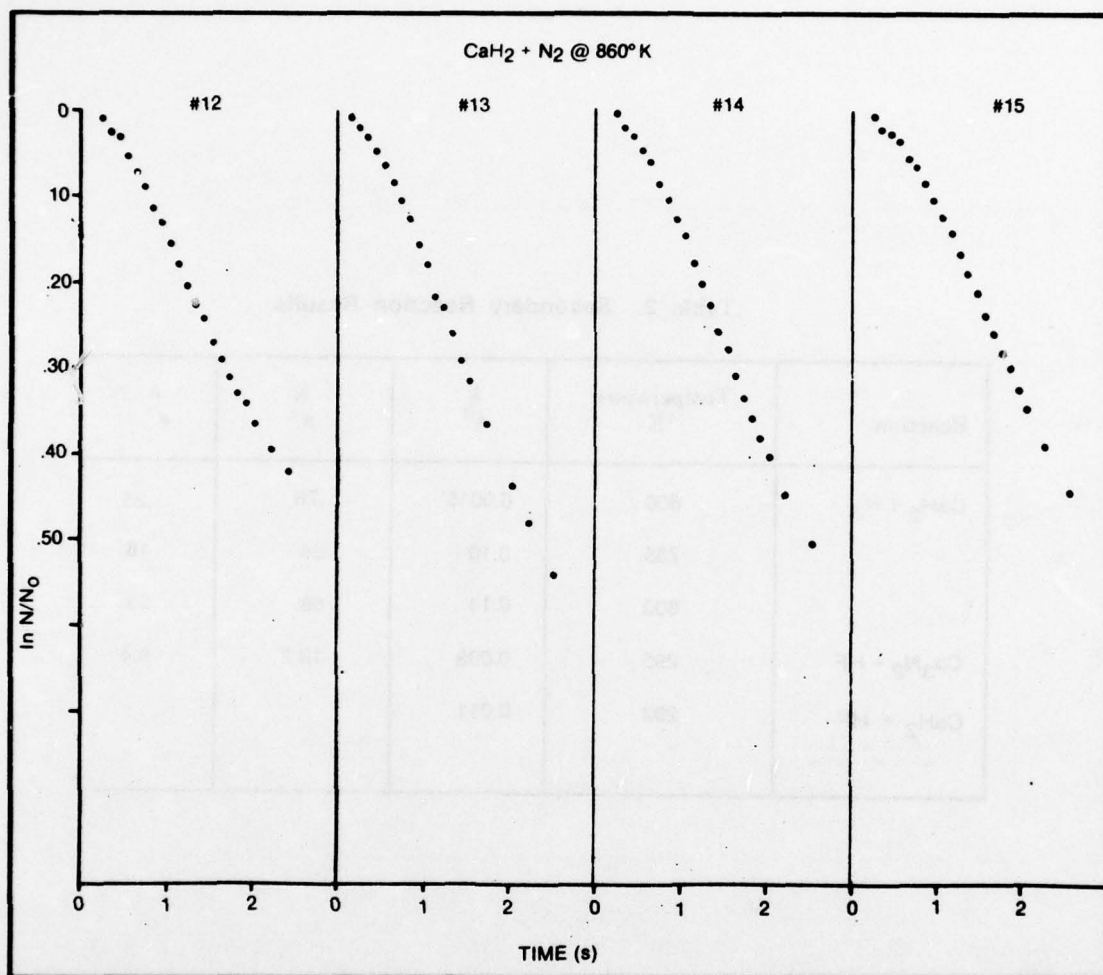


Figure 10. $\ln N/N_0$ versus time.

Table 2. Secondary Reaction Results

Reaction	Temperature °K	k s ⁻¹	K s ⁻¹	φ s ⁻¹
CaH ₂ + N ₂	600	0.0015	.76	.25
	755	0.10	54	18.
	800	0.14	69.	23.
Ca ₃ N ₂ + HF	295	0.038	19.2	6.4
CaH ₂ + HF	293	0.011		

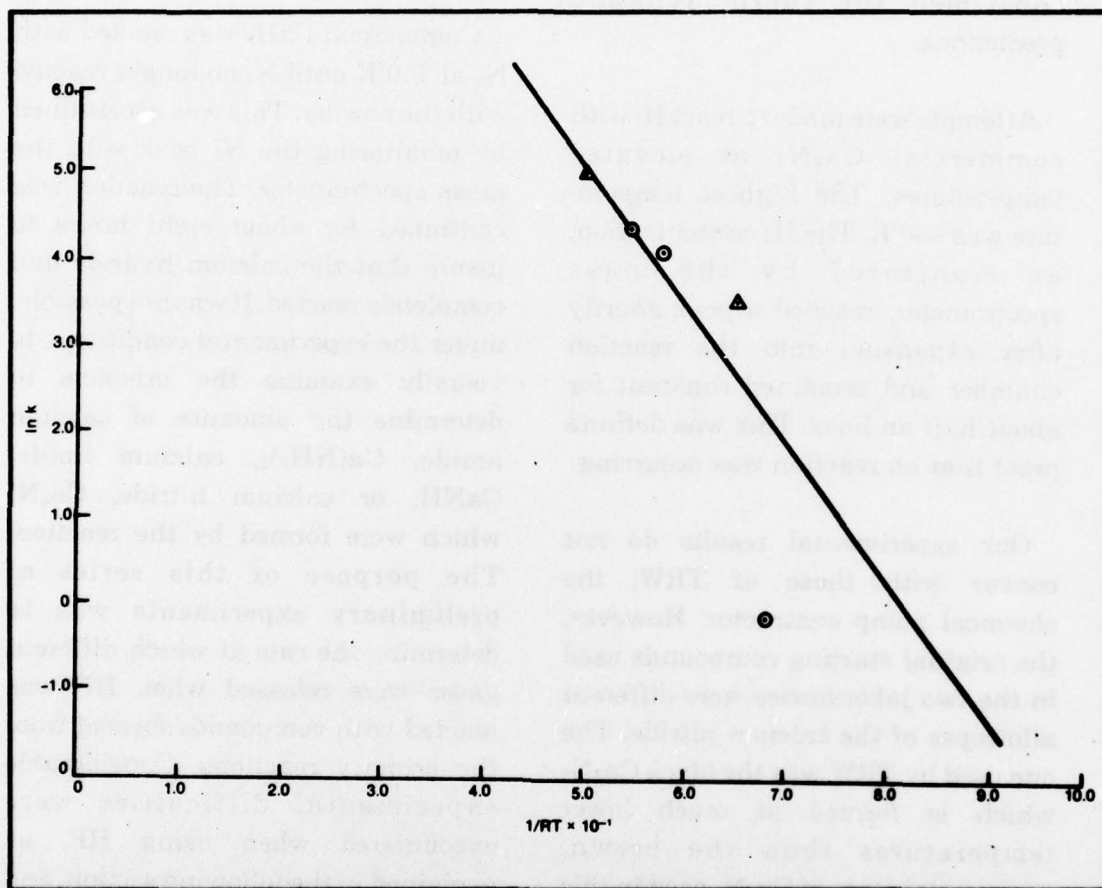


Figure 11. Arrhenius plot from $\text{CaH}_2 + \text{N}_2$ reaction.

B. $\text{Ca}_3\text{N}_2 + \text{H}_2$

Thermodynamic calculations indicate that the above reaction should not occur. Our experimental results confirmed the thermodynamic predictions.

Attempts were made to react H_2 with commercial Ca_3N_2 at elevated temperatures. The highest temperature was 830°K. The H_2 concentration, as monitored by the mass spectrometer, reached a peak shortly after expansion into the reaction chamber and remained constant for about half an hour. This was definite proof that no reaction was occurring.

Our experimental results do not concur with those of TRW, the chemical pump contractor. However, the original starting compounds used in the two laboratories were different allotropes of the calcium nitride. The one used by TRW was the black Ca_3N_2 which is formed at much lower temperatures than the brown, commercial form of Ca_3N_2 used in this laboratory. Furthermore, the experimental procedures used in the two laboratories were not the same.

C. $\text{CaH}_2 + \text{HF}$

Preliminary experiments were carried out at room temperature for the reaction of CaH_2 and HF. The result of

this preliminary study is presented in Table 2.

D. $\text{HF} + \text{Reaction Products From } \text{CaH}_2 + \text{N}_2$

Commercial CaH_2 was reacted with N_2 at 750°K until N_2 no longer reacted with the powder. This was ascertained by monitoring the N_2 peak with the mass spectrometer. The reaction was continued for about eight hours to insure that the calcium hydride had completely reacted. It was not possible, under the experimental conditions, to visually examine the products to determine the amounts of calcium amide, $\text{Ca}(\text{NH}_2)_2$, calcium imide, CaNH , or calcium nitride, Ca_3N_2 which were formed by the reaction. The purpose of this series of preliminary experiments was to determine the rate at which different gases were released when HF was reacted with compounds formed from the primary reactions. Considerable experimental difficulties were encountered when using HF, as explained in the following section, and study of the kinetics of this reaction was discontinued. The changes in concentration of various gases liberated during the room temperature reaction of HF with the products of the reaction of CaH_2 with N_2 is shown in Figure 12. No attempts were made to derive kinetics data because of the behavior of the HF concentration.

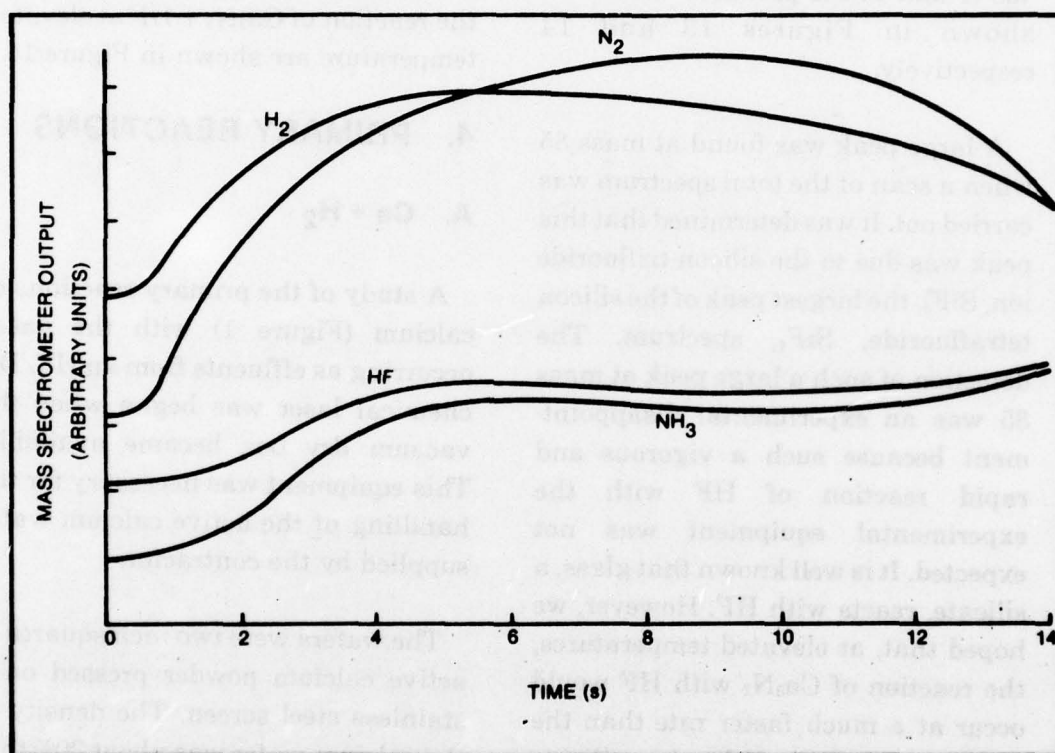


Figure 12. Reaction of HF with products of $CaH_2 + N_2$.

However, Figure 12 demonstrates the extreme usefulness of the mass spectrometer in these reaction rate experiments.

E. $\text{Ca}_3\text{N}_2 + \text{HF}$

The reaction of HF with Ca_3N_2 at 463°K and 673°K produced the traces shown in Figures 13 and 14 respectively.

A large peak was found at mass 85 when a scan of the total spectrum was carried out. It was determined that this peak was due to the silicon trifluoride ion, SiF_3^+ , the largest peak of the silicon tetrafluoride, SiF_4 , spectrum. The detection of such a large peak at mass 85 was an experimental disappointment because such a vigorous and rapid reaction of HF with the experimental equipment was not expected. It is well known that glass, a silicate, reacts with HF. However, we hoped that, at elevated temperatures, the reaction of Ca_3N_2 with HF would occur at a much faster rate than the reaction of HF with the silicate crucible. This was not the case at the elevated temperatures because the 85 peak increased almost as fast as the HF decreased. Thus, monitoring the HF peak to obtain a reaction rate with Ca_3N_2 was useless because some of the HF was being used to form SiF_4 . However, at room temperature, the rate of formation of SiF_3^+ was not

significant and the reaction rate was determined for the reaction of HF with Ca_3N_2 . Table 2 lists the reaction rate coefficient, k , the volume independent reaction rate coefficient, K , and the chemical reaction rate parameter, Φ , which were calculated from the room temperature reaction of HF with Ca_3N_2 [13]. Mass spectrometer outputs from the reaction of $\text{Ca}_3\text{N}_2 + \text{HF}$ at elevated temperature are shown in Figure 15.

4. PRIMARY REACTIONS

A. $\text{Ca} + \text{H}_2$

A study of the primary reactions of calcium (Figure 1) with the gases occurring as effluents from an HF/DF chemical laser was begun when the vacuum dry box became available. This equipment was necessary for the handling of the active calcium wafer supplied by the contractor.

The wafers were two inch squares of active calcium powder pressed on a stainless steel screen. The density of the calcium wafer was about 30% that of the theoretical density.

The use of the wafer necessitated modification in the reaction chamber. The wafer rested on an alumina coated heating element which was coiled in the shape of a pancake. Thermocouples were used to monitor the temperatures of the heater, the surface

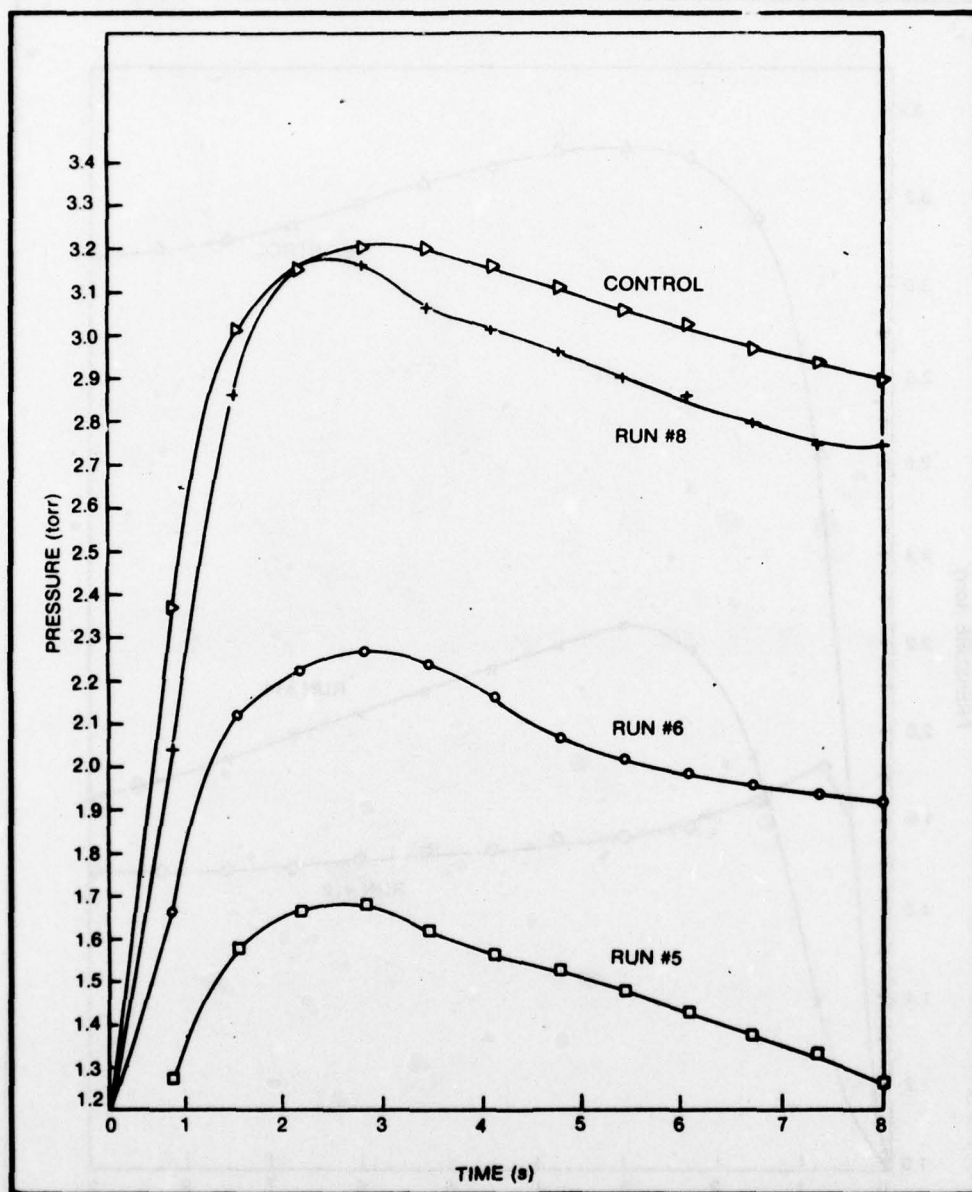


Figure 13. $\text{Ca}_3\text{N}_2 + \text{HF}$ @ 463°K.

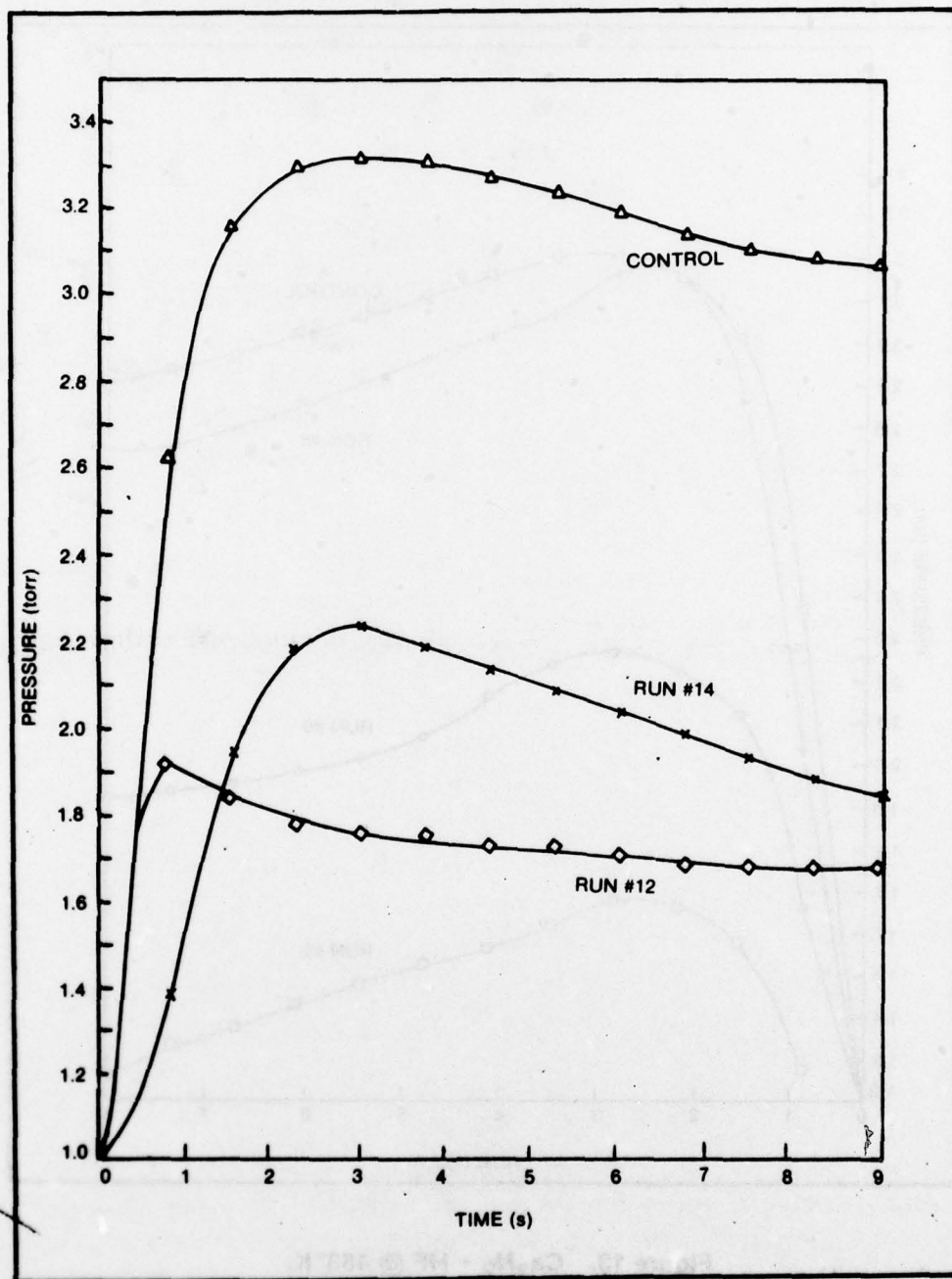


Figure 14. $\text{Ca}_3\text{N}_2 + \text{HF}$ @ 673°K .

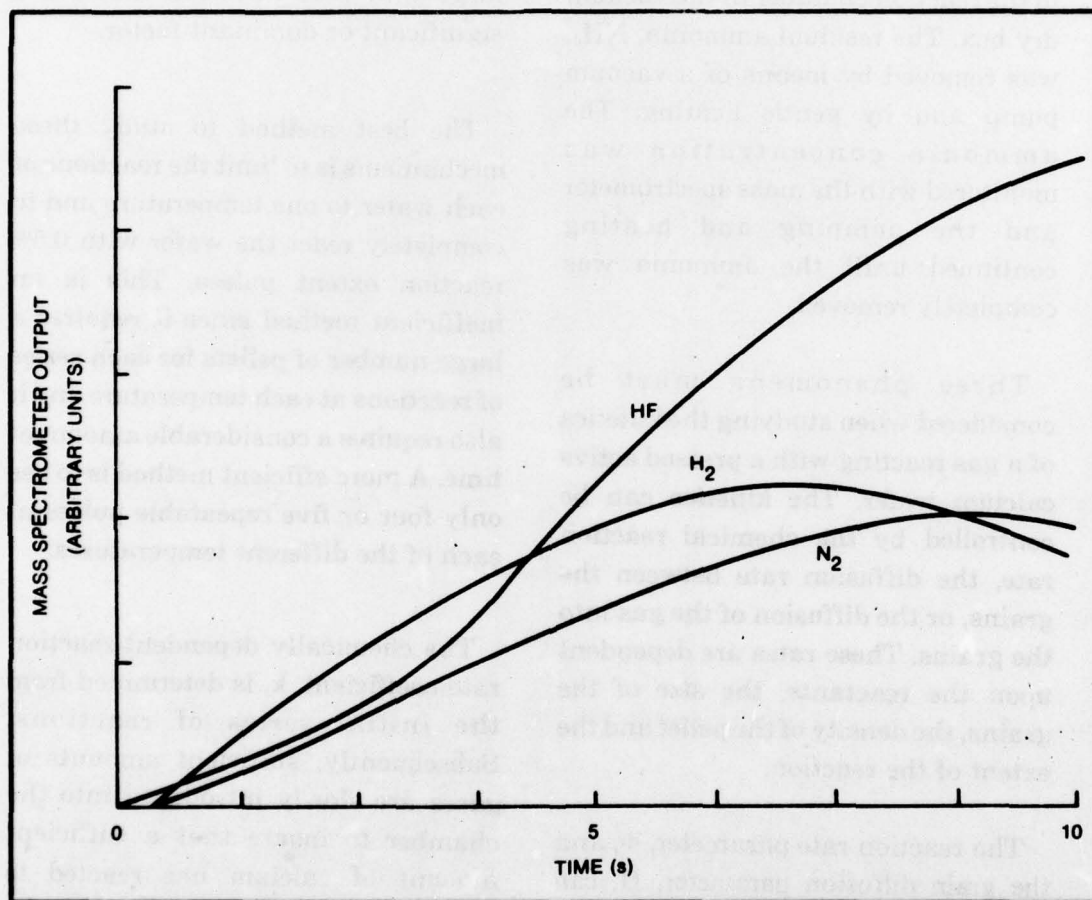


Figure 15. Reaction of HF with Ca_3N_2 .

of the calcium wafer and the temperature of the gas used in the reaction.

The calcium wafers were transferred to the reaction chamber in the vacuum dry box. The residual ammonia, NH_3 , was removed by means of a vacuum pump and by gentle heating. The ammonia concentration was monitored with the mass spectrometer and the pumping and heating continued until the ammonia was completely removed.

Three phenomena must be considered when studying the kinetics of a gas reacting with a pressed active calcium wafer. The kinetics can be controlled by the chemical reaction rate, the diffusion rate between the grains, or the diffusion of the gas into the grains. These rates are dependent upon the reactants, the size of the grains, the density of the pellet and the extent of the reaction.

The reaction rate parameter, Φ , and the grain diffusion parameter, Θ , can be experimentally determined from these measurements. At the beginning of the reaction sequence, the kinetics are determined only by the chemical reaction rate since no diffusion is necessary to reach unreacted surfaces. The pore diffusion characteristics have been experimentally determined and can be calculated. By using the

chemical pump model, and the experimentally determined Φ and calculated K , the solid grain diffusion rate can be determined when the extent of the reaction is sufficiently large that pore diffusion becomes a significant or dominant factor.

The best method to study these mechanisms is to limit the reactions of each wafer to one temperature and to completely react the wafer with 0.5% reaction extent pulses. This is an inefficient method since it requires a large number of pellets for each series of reactions at each temperature and it also requires a considerable amount of time. A more efficient method is to use only four or five repeatable pulses at each of the different temperatures.

The chemically dependent reaction rate coefficient, k , is determined from the initial series of reactions. Subsequently, sufficient amounts of gases are slowly introduced into the chamber to insure that a sufficient amount of calcium has reacted to realize a regime where grain diffusion is the dominant factor. The pore diffusion parameter is subsequently determined from measurements using a second series of pulses at different temperatures. The pore and grain diffusion must be insignificant during the initial test sequence. If not, k and, therefore Φ will not be accurate.

An isothermal series of reactions of H_2 with calcium was run at 650°K to experimentally determine the reaction extent at which diffusion affects the rate. The results showed that no apparent change occurred in the values of k up to 13.6% of the reaction extent. Thus, diffusion did not appear to have a significant effect. Values of 0.7795 sec^{-1} , 542 sec^{-1} and 296 sec^{-1} were calculated for k , K , and Φ respectively.

The next series of measurements for the $H_2 + Ca$ reaction was performed in the following manner:

(1) The initial reactions consumed 5% of the calcium and were conducted at three different temperatures.

(2) Sufficient gas was allowed to react so that a total of 20% of the calcium was reacted. Again a series of reactions was studied at three different temperatures and an additional 6% of the calcium was consumed.

(3) The reaction extent in the last series of reactions was between 40 and 43%.

The data was reduced with a Hewlett Packard 9810 programmable calculator with an attached digitizer and a digital plotter. A plot of $\ln N/N_0$ versus t was obtained from the

pressure gauge readings and the mass spectrometer readings. The reaction rate coefficient, k , was also obtained. An example of the plot is shown in Figure 16. The data obtained from the mass spectrometer and the pressure gauge are in good agreement.

No apparent effect of the temperature on the reaction rate was observed when the data from the experiments just described was analyzed. Obviously, the fact is contrary to the Arrhenius theory. The only correlation of reaction rate and temperature that could explain our finding is that the rate decreases considerably as the reaction extent increases. This correlation is shown in Figure 17. The increase in precision with an increase in reaction extent is expected because diffusion rates are less sensitive to experimental parameters than reaction rates. The effect of diffusion becomes more prominent as the extent increases.

Each point on the curve is the average value at a given temperature. The crosses represent the mass spectrometer data and the circles represent the data from the pressure gauge.

An interpretation of the rate versus temperature behavior is that the calcium pellets did not reach thermal

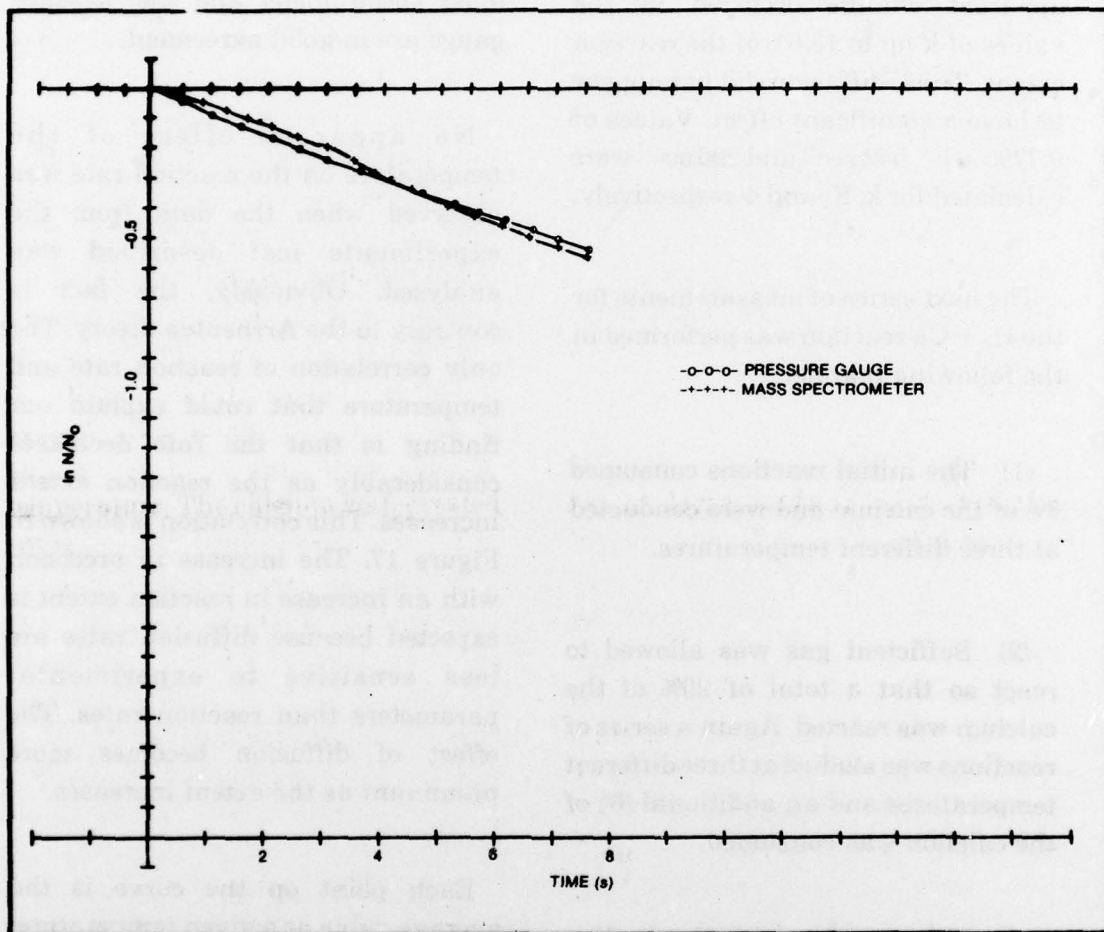
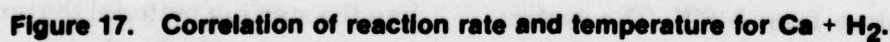


Figure 16. $\ln N/N_0$ versus time for $\text{Ca} + \text{H}_2$.



equilibrium and that the heater temperature is not an accurate indication of the reaction temperature.

B. $\text{Ca} + \text{N}_2$

The results from the $\text{Ca} + \text{H}_2$ experiments indicated that no diffusion effects were detectable in the first 14% of reaction extent. A test plan which studied the reactions at different temperatures, substituting N_2 for H_2 , was begun assuming that the nitrogen would behave similarly to H_2 in the first 5 to 6% of reaction extent. A different "sandwich" heating system was fabricated in order to obtain a more uniform calcium temperature. The calcium wafer rested between two heating elements. The heating elements were encased in a thin coating of high temperature ceramic.

The data obtained at 548°K was extremely reproducible and all the thermocouple readings were in agreement, indicating that thermal equilibrium was achieved.

The heating element burned out in the process of increasing the temperature from 548°K. The system was cooled and a new heating element fabricated and inserted into the system. Another series of experiments were then carried out at 611°K. A large decrease in reaction rate was observed

when the results were compared to those obtained at 548°K. The results at 548°K gave a Φ value of 14.7 s^{-1} and this value is in very good agreement with the one reported by the contractor whose value was 29 s^{-1} . However, the data at 611°K gave a value of 2.4 s^{-1} as compared to the expected value of about 90 s^{-1} . Thus, the value at 611°K was smaller than the value at 548°K by a factor of 8. It was postulated that a physical change in the calcium could have occurred during the temperature cycling and that this change was the reason for the puzzling results. The pumping ability of the chemical pump could be reduced considerably on a restart if the temperature cycling effect is a true effect. Continued investigations of this phenomenon were not pursued because of equipment malfunction and time limitations. Another explanation of the described effect involves the consideration of the molecular volume for each of the compounds, Ca , CaH_2 , Ca_3N_2 , and CaF_2 . The molecular volume, found from the density, is presented in Table 3. The solid grain will swell or shrink depending upon whether the reaction product has a larger or smaller molar volume. If the molar volume is larger than the starting material the product formed would shield the unreacted interior from the gases. More surface would become available for gas reaction if the molar volume is smaller, because of shrinkage and crack

Table 3. The Molar Volumes of Chemical Pump Compounds

Molar Volumes	
Compound	Molecular Volume (cm ³)
Ca	26.0
CaH ₂	22.2
Ca ₃ N ₂	56.4
CaF ₂	24.6

formation. Calcium nitride (Ca_3N_2) has a much larger molar volume than the other products and thus, this physical change may help explain some of our findings. However, we have no experimental evidence to support any explanation based on molecular volume consideration.

5. PLANNED WORK

Considerable time and effort was devoted to designing, modifying and assembling equipment in order that better experimental results could be obtained.

A new cross was designed and is shown in Figure 18. The use of quartz windows would allow one to visually observe any changes in the solids involved in the reactions. The windows would have been replaced by stainless steel plates when the use of HF was contemplated.

The modified time of flight mass spectrometer is shown in Figure 18.

This instrument with its molecular beam inlet system would have allowed the use of higher gas pressures and flows than the ones described in this report.

A large reaction chamber, originally fabricated to study gas, liquid and solid propellant combustion is shown in Figure 19. The use of this chamber would have allowed the use of larger amounts of calcium. Thus, the connection of this chamber to the mass spectrometer and the monitoring of all the gases in the reaction would have unveiled the actual kinetics and mechanisms which are involved when a real calcium chemical pump is used.

A data acquisition and reduction system was also purchased. This equipment would have permitted more accurate and more rapid analysis than the outdated, slow, and manual techniques used in the present investigations.



Figure 18. The modified time of flight mass spectrometer for $\text{Ca} + \text{H}_2$.

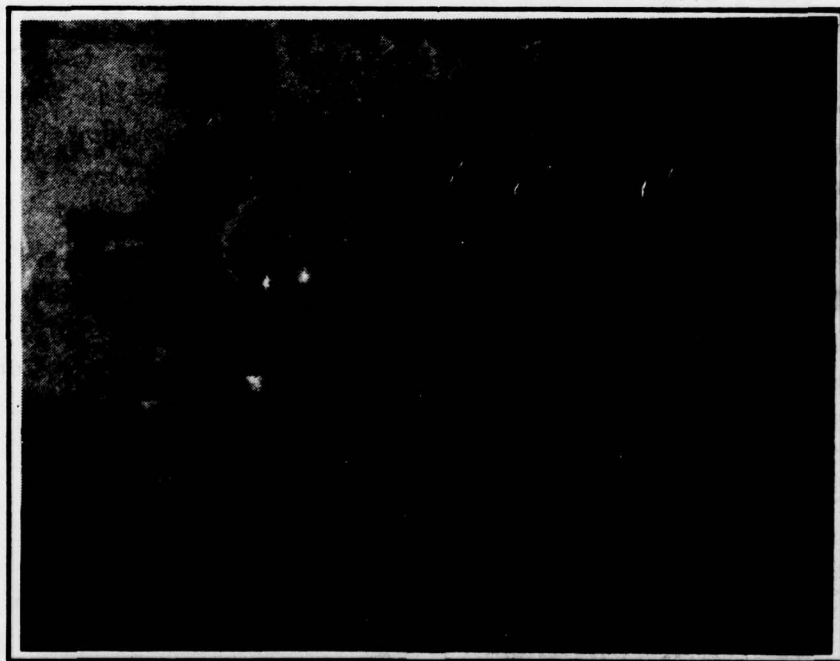


Figure 19. Large Reaction Chamber

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